

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-202684

(43)Date of publication of application : 05.08.1997

(51)Int.Cl.

C30B 15/00
C30B 29/06
H01L 21/208

(21)Application number : 08-026021

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(22)Date of filing : 19.01.1996

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(54) PRODUCTION OF SILICON SINGLE CRYSTAL HAVING FEW CRYSTAL DEFECT AND SILICON SINGLE CRYSTAL OBTAINED BY THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a silicon single crystal by a Czochralski method improved in withstand voltage of oxide film.

SOLUTION: In this method for producing a silicon single crystal by a Czochralski method, a time in which the silicon single crystal to be grown passes a temperature range from 1,250° C to 1,200° C in crystal growth is adjusted to ≥ 10 minutes and ≤ 20 minutes. The single crystal is produced by such a method in this inventions.

LEGAL STATUS

[Date of request for examination] 17.03.2000

[Date of sending the examiner's decision of rejection] 20.05.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-202684

(43) 公開日 平成9年(1997)8月5日

(51) Int.Cl. ⁸	識別記号	庁内整理番号	F I	技術表示箇所
C 3 0 B 15/00			C 3 0 B 15/00	P
29/06	5 0 2		29/06	5 0 2 E
H 0 1 L 21/208			H 0 1 L 21/208	P

審査請求 未請求 請求項の数3 F D (全 7 頁)

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(54) 【発明の名称】 結晶欠陥が少ないシリコン単結晶の製造方法およびこの方法で製造されたシリコン単結晶

(57) 【要約】 (修正有)

【課題】 酸化膜耐圧を改善したチョクラスキー法によるシリコン単結晶を、高生産性で製造する。

【解決手段】 チョクラスキー法によってシリコン単結晶を製造する場合において、育成されるシリコン単結晶が結晶成長時に、1250℃から1200℃までの温度域を通過する時間が10分以上20分以下となるようにすることを特徴とする、シリコン単結晶の製造方法。およびこの方法によって製造されたシリコン単結晶。

【特許請求の範囲】

【請求項1】 チョクラスキー法によってシリコン単結晶を製造する場合において、育成されるシリコン単結晶が結晶成長時に、1250℃から1200℃までの温度域を通過する時間が20分以下となるようにすることを特徴とする、シリコン単結晶の製造方法。

【請求項2】 チョクラスキー法によってシリコン単結晶を製造する場合において、育成されるシリコン単結晶が結晶成長時に、1250℃から1200℃までの温度域を通過する時間が10分以上20分以下となるようにすることを特徴とする、シリコン単結晶の製造方法。

【請求項3】 請求項1または請求項2に記載した方法によって製造されたシリコン単結晶。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸化膜耐圧を改善したチョクラスキー法によるシリコン単結晶を、高生産性で製造する方法に関する。

【0002】

【従来の技術】近年は、半導体回路の高集積化に伴う素子の微細化により、MOS-LSIのゲート電極部の絶縁酸化膜はより薄膜化されており、このような薄い絶縁酸化膜においてもデバイス素子動作時に絶縁耐圧が高いこと、リーク電流が小さいことすなわち、酸化膜の信頼性が高いことが要求されている。

【0003】この点、チョクラスキー法(Czochralski法、以下CZ法という。)によるシリコン単結晶より製造されたシリコンウェーハの酸化膜耐圧は、浮遊帯溶融法(Floating Zone法、FZ法という。)によるシリコン単結晶より製造されたウェーハや、CZ法によるウェーハ上にシリコン単結晶薄膜を成長させたエピタキシャルウェーハの酸化膜耐圧に比べて著しく低いことが知られている(「サブミクロンデバイスII、3ゲート酸化膜の信頼性」、小柳光正、丸善(株)、P70)。

【0004】このCZ法において酸化膜耐圧を劣化させる主な原因は、シリコン単結晶育成時に導入される結晶欠陥によることが判明しており、結晶成長速度を極端に低下(例えば0.4mm/min以下)させることで、CZ法によるシリコン単結晶の酸化膜耐圧を著しく改善できることも知られている(例えば、特開平2-267195号公報参照)。しかし、酸化膜耐圧を改善するために、単に結晶成長速度を従来の1mm/min以上から、0.4mm/min以下に低下させたのでは、酸化膜耐圧は改善できるものの、単結晶の生産性が半分以上となり、著しいコストの上昇をもたらしてしまう。

【0005】

【発明が解決しようとする課題】本発明は、このような問題点を鑑みなされたもので、酸化膜耐圧を改善したチョクラスキー法によるシリコン単結晶を、高生産性で

得ることを目的とする。

【0006】

【課題を解決するための手段】上記課題を解決するため、本発明者らは、CZ法によるシリコン単結晶成長時に、その成長単結晶が受けた熱履歴と、導入された結晶欠陥との関係を種々、調査、検討した結果本発明を完成したもので、本発明の請求項1に記載した発明は、チョクラスキー法によってシリコン単結晶を製造する方法において、育成されるシリコン単結晶が結晶成長時に、1250℃から1200℃までの温度域を通過する時間が20分以下となるようにすることを特徴とする。このようなCZ法によるシリコン単結晶の成長時の熱履歴とすれば、酸化膜耐圧を劣化させる結晶欠陥の欠陥核の形成が阻害され、育成単結晶中に導入される結晶欠陥密度を減少させることができ、著しくシリコン単結晶の酸化膜耐圧の改善ができる。しかも、結晶成長速度を極端に低下させたり、一定の温度領域を徐冷させるといった、単結晶の生産性を悪化させるような方法を用いる必要はなく、超高速引き上げが可能であるため、単結晶の生産性を飛躍的に向上させることができる。

【0007】また、本発明の請求項2に記載した発明は、チョクラスキー法によってシリコン単結晶を製造する方法において、育成されるシリコン単結晶が結晶成長時に、1250℃から1200℃までの温度域を通過する時間が10分以上20分以下となるようにすることを特徴とする。このように、請求項1の発明に対し1250℃から1200℃までの温度域を通過する時間の下限値を限定したのは、一般のCZ法による引上装置での単結晶の育成において、容易に達成が可能な、発明のより好適とされる範囲を明示したものである。従って、請求項2により請求項1に記載した発明の範囲が限定されるものではない。

【0008】さらに、本発明の請求項3に記載した発明は、請求項1または請求項2に記載した方法によって製造されたシリコン単結晶である。前記請求項1および請求項2に記載した方法では、酸化膜耐圧を劣化させる結晶欠陥の欠陥核がそもそも形成されにくいため、確実に酸化膜耐圧を改善したシリコン単結晶を製造することができる。

【0009】以下、本発明を更に詳細に説明するが、説明に先立ち各用語につき予め解説しておく。

1) FPD(Flow Pattern Defect)とは、成長後のシリコン単結晶棒からウェーハを切り出し、表面の歪み層を沸酸と硝酸の混合液でエッチングして取り除いた後、 $K_2Cr_2O_7$ と弗酸と水の混合液で表面をエッチングすることによりピットおよびさざ波模様が生じる。このさざ波模様をFPDと称し、ウェーハ面内のFPD密度が高いほど酸化膜耐圧の不良が増える(特開平4-192345号公報参照)。

2) LSTD(Laser Scattering

Tomography Defect) とは、成長後のシリコン単結晶棒からウェーハを切り出し、表面の歪み層を弗酸と硝酸の混合液でエッチングして取り除いた後、ウェーハを劈開する。この劈開面より赤外光を入射し、ウェーハ表面から出た光を検出することでウェーハ内に存在する欠陥による散乱光を検出することができる。ここで観察される散乱体については学会等ですでに報告があり、酸素析出物とみなされている(J. J. A. P. Vol. 32, P3679, 1993参照)。

【0010】これらFPD、LSTDの欠陥密度は酸化膜耐圧の不良率と強い相関があることから、共に酸化膜耐圧劣化因子と考えられている。従って、CZ法によるシリコン単結晶の酸化膜耐圧を改善するためには、このFPD、LSTD欠陥を減少させる必要がある。

【0011】本発明者らは、低速成長させると何故、FPD、LSTDが減少し、酸化膜耐圧が良くなるのかを解明すべく、徐冷型・急冷型の二種類の炉内構造下において、結晶成長時に成長速度を高速から低速に急変させてみたところ、FPD、LSTDの欠陥密度は成長速度変化点からではなく、それ以前(既成長部)で急激に低下していた。この変化した位置は炉内構造によって異なり、急冷型構造下では成長速度変化点の手前約14~11cmの間(図1(a)のA点からB点)、また徐冷型構造下では同じく成長速度変化点の手前約19~16cmの間(図1(a)のA'点からB'点)であった。ところが、この位置に相当する結晶温度は、ほぼ同じく1150℃~1080℃の温度帯に相当することがわかった(図1(b)参照)。

【0012】このことは、結晶欠陥消滅過程として、シリコン単結晶成長中における1150℃~1080℃の温度帯が影響することを意味している。すなわち、単結晶の成長速度を極端に低下させれば、成長中の結晶がすべての温度領域で通過時間が長くなり、結果として1150℃~1080℃の温度域の通過時間も長くなるため、FPD、LSTD欠陥が消滅過程をへることによって、酸化膜耐圧が改善されるのである。

【0013】従って、1150℃~1080℃の温度域の通過時間さえ長くすることが出来れば、FPD、LSTD欠陥を消滅させることができ、その他の温度領域、特に結晶成長速度に直接的に影響する結晶成長界面近傍の高温度域の通過時間を長くする必要はなく、成長界面近傍の温度勾配をよりきつくすることで、結晶成長速度を低速度とせず、したがって単結晶の生産性を落とすことなく、酸化膜耐圧の改善ができることを解明し、先に提案した(特願平7-143391号)。

【0014】しかし、上述のように酸化膜耐圧を劣化させるFPD、LSTD欠陥の消滅過程は解明したものの、これらの欠陥核の発生・形成については不明であり、これを解明し、欠陥核そのものの形成を抑制することができれば、CZ法によるシリコン単結晶のより完全

な酸化膜耐圧の改善を図ることができる。また、上記一定の温度領域を徐冷するという方法では、従来に比し引上速度をそれほど落とさないで済むとは言え、実際問題従来法以上の引上速度、生産性を望むことは困難である。

【0015】そこで、本発明者らはさらに、酸化膜耐圧劣化因子となる欠陥の欠陥核発生そのものの温度領域を調査・解明し、欠陥核の形成を抑制するとともに、結晶成長速度を従来より高速とし、シリコン単結晶の一層の高品質化と高生産性の達成を図ることを検討した。

【0016】しかして、本発明者らはこれを解明すべく、さらに結晶成長時に成長速度を中速から超高速に急変させる実験を行った。すると、FPD、LSTDの欠陥密度は成長速度変化点からではなく、それ以前(既成長部)で急激に増加していた。この変化した位置は、成長速度変化点の手前約22~16cmの間(図2(a)のC点からD点)であった。そして、この位置に相当する結晶温度は、上述の実験から得られた1150℃~1080℃の温度帯に相当するものである(図2(b)参照)。すなわち、1150℃~1080℃の温度域を急冷しはじめる結晶位置から、欠陥密度が増加しており、上記実験結果が正しいことを再確認できた。

【0017】ところが、結晶の引き上げをそのまま継続すると、その後再び欠陥密度が減少する挙動が確認された。この欠陥が減少した位置は、成長速度変化点の手前約12~9cmの間(図2(a)のE点からF点)であった。そして、この位置に相当する結晶温度は、1250℃~1200℃の温度帯に相当するものであることがわかった(図2(b)参照)。

【0018】このことは、結晶欠陥核の形成過程として、シリコン単結晶成長中における1250℃~1200℃の温度帯が影響することを意味している。すなわち、単結晶の成長時において導入される、酸化膜耐圧を劣化させるFPD、LSTD欠陥は、1250℃~1200℃の温度領域でその核が形成され、1150℃~1080℃の温度領域で消滅過程をたどるのである。よって、CZ法によるシリコン単結晶の酸化膜耐圧をより確実に解決するためには、結晶成長時にFPD、LSTDの欠陥核を形成させないようにする為に、1250℃~1200℃の温度域を出来るだけ急冷し、その通過時間を短くすれば良いことになる。

【0019】これを確認すべく本発明者らは更に、各種炉内構造下で同様な実験を行い、FPD欠陥密度と結晶成長時の1250℃~1200℃までの温度域通過時間との関係を調査したところ、図3に示したような結果が得られた。この図を見ると、1250℃~1200℃までの温度域を通過する時間が20分以下の結晶では、例外なく欠陥密度が少なく酸化膜耐圧が改善された結晶が育成されることがわかる。従って、酸化膜耐圧劣化因子たるFPD、LSTD欠陥の欠陥核は1250℃~12

00℃の温度域で形成され、この温度域を通過する時間が20分以下となると、欠陥核が十分に形成されないために、結果として出来た結晶の欠陥密度が減少するのである。

【0020】一方、1250℃～1200℃の温度域を通過する時間が20分を越えると、欠陥密度のばらつきが大きいものの、徐々に欠陥密度が減少する傾向がある。これは1250℃～1200℃の温度域を徐冷されたために、多数の欠陥核が形成され、全体的に欠陥密度が増加するが、1250℃～1200℃の通過時間が長いものは、その後前記1150℃～1080℃の温度域も徐冷され、欠陥消滅過程をたどるため、徐々に欠陥密度の少ない結晶となるのである。

【0021】このように本発明によれば、シリコン単結晶中の結晶欠陥は、その核そのものが形成される温度である1250℃～1200℃の温度域を急冷される為に、欠陥核形成反応が十分でなく、その形成が阻害される。結晶中に欠陥核が形成されていなければ、その後の熱履歴、特に結晶欠陥消滅過程の温度域たる1150℃～1080℃の履歴がいかなるものであろうとも、絶対的な結晶欠陥の密度を減少させることが可能であり、酸化膜耐圧特性に優れた高品質のシリコン単結晶の製造が可能となる。さらに、本発明では、従来の極端に引上速度を低下させる方法とは全く逆に、極端に引上速度を上げるものであり、また一定の温度域を徐冷する必要もないため、単結晶の飛躍的な生産性の向上を図ることが出来る。

【0022】

【発明の実施の形態】以下、本発明の実施形態について、図面を参照しながら詳細に説明する。まず、CZ法による単結晶引上装置の構成例を図4により説明する。図4に示すように、この単結晶引上装置100は、チャンバ101と、チャンバ101中に設けられたルツボ102と、ルツボ102の周囲に配置されたヒータ105と、ルツボ102を回転させるルツボ保持軸107及び回転機構108と、シリコンの種子結晶Sを保持するシードチャック22と、シードチャック22を引き上げるケーブル1と、ケーブル1を回転又は巻き取る巻取機構109を備えて構成されている。ルツボ102の内側の融液Lを収容する側には石英ルツボ103が設けられ、石英ルツボ103の外側には黒鉛ルツボ104が設けられている。また、ヒータ105の外側周囲には断熱材106が配置されている。更に、炉内のガスの流れを整え、発生するSiO等の反応ガスを有効に排出するため成長単結晶を囲繞するように整流筒2が設けられる場合もある。また、最近ではチャンバ101の水平方向の外側に、図示しない磁石を設置し、シリコン融液Lに水平

方向の磁場を印加することによって、融液Lの対流を抑制し、単結晶の安定成長をはかる、いわゆるMCZ法が用いられることも多い。

【0023】次に、上記の単結晶引上装置100による単結晶育成方法について説明する。まず、ルツボ102内でシリコンの高純度多結晶原料を融点(約1400℃)以上に加熱して融解する。次に、ケーブル1を巻き出すことにより融液Lの表面略中心部に種子結晶Sの先端を接触又は浸漬させる。その後、ルツボ保持軸107を適宜の方向に回転させるとともに、ケーブル1を回転させながら巻き取り種子結晶Sを引き上げることににより、単結晶育成が開始される。以後、引上速度と温度を適切に調節することにより略円柱形状の単結晶棒Cを得ることができる。

【0024】この場合、本発明のように1250℃～1200℃の温度域を通過する時間を20分以下として単結晶の酸化膜耐圧を改善し、かつ単結晶の生産性を飛躍的に向上させるためには、従来に比し超高速度で引き上げる必要がある。そこで、本発明を実施するための炉内構造は、炉内のガスの流れを整え、発生するSiO等の反応ガスを有効に排出するとともに、成長単結晶Cを冷却し、単結晶への輻射熱を遮ることによって、結晶成長速度を高速化することを可能とするため、その下端部を融液面に近接させた整流筒2が、成長単結晶を囲繞するように設けられている。このような整流筒を設けることによって、引上装置の上部より導入されるAr等の不活性ガスは、整流筒によってその流路が規定され、成長単結晶に向けて集中して流れるため、結晶を冷却する効果が大きい。しかも、このような整流筒は原料融液面やルツボ内壁、さらにはヒータ等からの輻射熱をカットすることも出来ることから、より単結晶の高速成長が可能となる。

【0025】

【実施例】以下、本発明の実施例を示す。

(実施例) 図4に示した整流筒を具備する引上装置で、20インチ石英ルツボに原料多結晶シリコンを60Kgチャージし、直径6インチ、方位<100>のシリコン単結晶棒を1.6mm/minの平均引上速度で育成した(単結晶棒の直胴長さ約85cm)。この単結晶棒から、ウエーハを切り出し、鏡面加工を施すことによって、シリコン単結晶の鏡面ウエーハを作製した。こうして出来たシリコン単結晶の鏡面ウエーハにつき、前記F-PD、LSTD欠陥の測定を行った。その測定結果を下記の表1に示した。表には従来のCZ法による欠陥密度の典型例を、比較のため併記した。

【0026】

【表1】

	平均成長速度 (mm/min)	F P D (ヶ/cm ²)	LSTD (ヶ/cm ²)
実施例	1.60	$\bar{X}=180$ $n=10$	$\bar{X}=2.8 \times 10^6$
比較例 (従来法)	1.00	$\bar{X}=650$ $n=18$	$\bar{X}=2.0 \times 10^6$

【0027】なお、本発明は、上記実施形態に限定されるものではない。上記実施形態は、例示であり、本発明の特許請求の範囲に記載された技術的思想と実質的に同一な構成を有し、同様な作用効果を奏するものは、いかなるものであっても本発明の技術的範囲に包含される。

例えば、上記実施形態においては、直径6インチのシリコン単結晶を育成する場合につき例を挙げて説明したが、本発明はこれには限定されず、1250℃～1200℃の温度域を通過する時間を20分以下とすれば、同様の作用効果は、直径8～16インチあるいはそれ以上のシリコン単結晶にもあてはまる。

【0028】また、上記実施形態では、単結晶の成長速度を超高速とするため、整流筒を用いたが、本発明はこれには限定されず、成長結晶の冷却速度を上げまたは放射熱を有効に遮蔽することが出来るものであるならば、どのような炉内構造としても良い。例えば、ルツボとルツボ内の融液を部分的にカバーして放射熱を遮断してもよいし、前記整流筒の下端部に、より冷却効果を増すため、熱遮蔽体を設置してもよい。

【0029】

【発明の効果】以上説明したように、本発明により、CZ法によって製造されるシリコン単結晶のF P D、L S T D欠陥を減少させ、酸化膜耐圧の優れた高品質の結晶を得ることが出来る。しかも本発明では、引上速度を極端に低下したり、一定の温度領域の徐冷化等は必要ではなく、超高速度で結晶を引き上げるため、単結晶の生産性を飛躍的に向上させることができる。

【図面の簡単な説明】

【図1】(a) 結晶成長中、成長速度を低速に急変化させた場合における、結晶位置とF P D欠陥密度との関係を示した図である。

(b) 湯面からの距離と結晶温度との関係を示した図である。

【図2】(a) 結晶成長中、成長速度を高速に急変化させた場合における、結晶位置とF P D欠陥密度との関係を示した図である。

(b) 湯面からの距離と結晶温度との関係を示した図である。

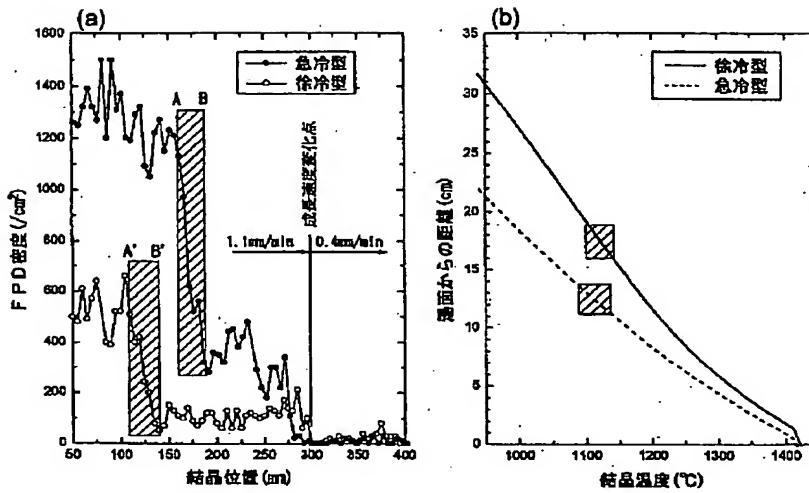
【図3】1250℃から1200℃までの通過時間とF P D欠陥密度との関係を示した図である。

【図4】CZ法による単結晶引上装置の断面概略図である。

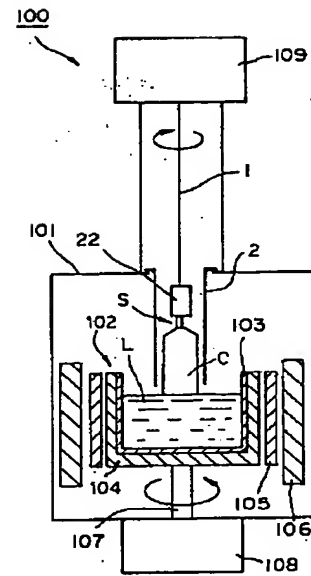
【符号の説明】

- | | |
|-------------|-----------|
| 1 ケーブル | 2 整流筒 |
| 22 シードチャック | |
| 100 単結晶引上装置 | 101 チャンバ |
| 102 ルツボ | 103 石英ルツボ |
| 104 黒鉛ルツボ | 105 ヒータ |
| 106 断熱材 | 107 ルツボ保 |
| 30 持軸 | |
| 108 回転機構 | 109 巻取機構 |
| C 成長単結晶 | |
| L シリコン融液 | |
| S 種子結晶 | |

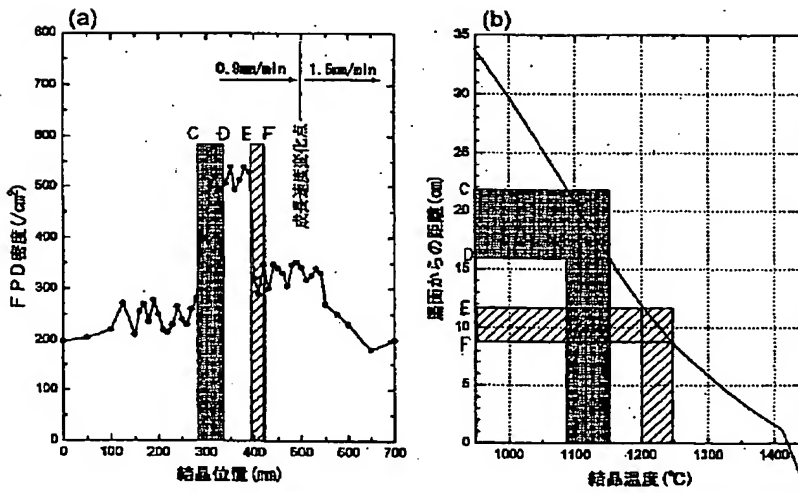
【図1】



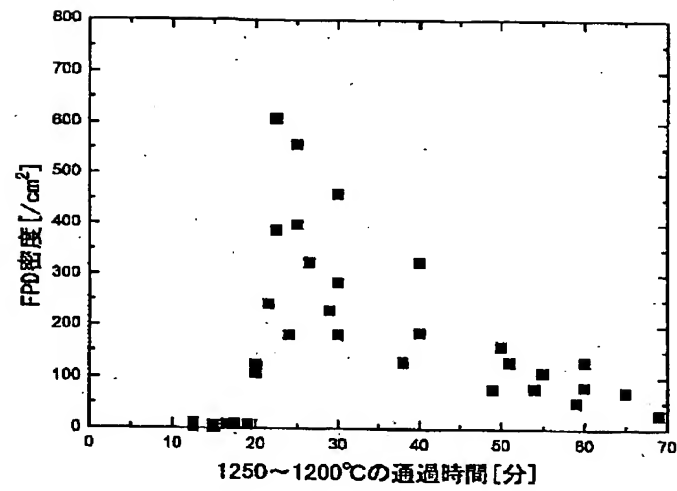
【図4】



【図2】



【図3】



フロントページの続き

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PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-202684

(43)Date of publication of application : 05.08.1997

(51)Int.Cl.

C30B 15/00
C30B 29/06
H01L 21/208

(21)Application number : 08-026021

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(22)Date of filing : 19.01.1996

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(54) PRODUCTION OF SILICON SINGLE CRYSTAL HAVING FEW CRYSTAL DEFECT AND SILICON SINGLE CRYSTAL OBTAINED BY THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a silicon single crystal by a Czochralski method improved in withstand voltage of oxide film.

SOLUTION: In this method for producing a silicon single crystal by a Czochralski method, a time in which the silicon single crystal to be grown passes a temperature range from 1,250°C to 1,200°C in crystal growth is adjusted to ≥ 10 minutes and ≤ 20 minutes. The single crystal is produced by such a method in this inventions.

LEGAL STATUS

[Date of request for examination] 17.03.2000

[Date of sending the examiner's decision of rejection] 20.05.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of a silicon single crystal characterized by making it the time amount to which the silicon single crystal raised when manufacturing a silicon single crystal with the Czochralski method passes through the temperature region from 1250 degrees C to 1200 degrees C at the time of crystal growth become 20 or less minutes.

[Claim 2] The manufacture approach of a silicon single crystal characterized by making it the time amount to which the silicon single crystal raised when manufacturing a silicon single crystal with the Czochralski method passes through the temperature region from 1250 degrees C to 1200 degrees C at the time of crystal growth become 20 or less minutes 10 minutes or more.

[Claim 3] The silicon single crystal manufactured by the approach indicated to claim 1 or claim 2.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing the silicon single crystal by the Czochralski method which has improved oxide film pressure-proofing by the sex from Takao.

[0002]

[Description of the Prior Art] The insulating oxide film of the gate polar zone of MOS-LSI is thin-film-ized more by detailed-ization of the component accompanying high integration of a semiconductor circuit in recent years, and it is required also in such a thin insulating oxide film at the time of device component actuation that withstand voltage is high and that leakage current should be small, i.e., the dependability of an oxide film is high.

[0003] Oxide-film pressure-proofing of the silicon wafer manufactured from the silicon single crystal by this point and the Czochralski method (it is called the Czochralski method and a following CZ process.) FZ method (it is called the Floating Zone method and an FZ method.) The remarkably low thing is known compared with oxide film pressure-proofing of the wafer manufactured from the silicon single crystal to twist, and the epitaxial wafer which grew up the silicon single crystal thin film on the wafer by the CZ process (it "submicron-device-II(s)). The dependability of 3 gate oxide", Mitsumasa Koyanagi, Maruzen Co., Ltd., P70.

[0004] The main causes of degrading oxide-film pressure-proofing in this CZ process are it having become clear that it is based on the crystal defect introduced at the time of silicon single crystal training, and reducing the rate of crystal growth extremely (for example, 0.4 or less mm/min), and it is known that oxide-film pressure-proofing of the silicon single crystal by the CZ process will also be remarkably improvable (for example, refer to JP,2-267195,A). However, although it can be improved by oxide-film pressure-proofing in having only reduced the rate of crystal growth to conventional 1 mm/min, as mentioned above 0.4 mm/min or less in order to improve oxide-film pressure-proofing, the productivity of a single crystal will become below one half, and the remarkable rise of cost will be brought about.

[0005]

[Problem(s) to be Solved by the Invention] This invention was made in view of such a trouble, and aims at obtaining the silicon single crystal by the Czochralski method which has improved oxide film pressure-proofing by the sex from Takao.

[0006]

[Means for Solving the Problem] It is what completed this invention as a result of this invention persons' investigating and considering various relation between the heat history which the growth single crystal received at the time of the silicon single crystal growth by the CZ process, and the introduced crystal defect, in order to solve the above-mentioned technical problem. Invention indicated to claim 1 of this invention is characterized by making it the time amount to which the silicon single crystal raised in the approach of manufacturing a silicon single crystal, by the Czochralski method passes through the temperature region from 1250 degrees C to 1200 degrees C at the time of crystal growth become 20 or less minutes. Formation of the heat history at the time of growth of the silicon single crystal by such CZ process, then the defective nucleus of the crystal defect which degrades oxide-film pressure-proofing is checked, the crystal defect consistency introduced into a training single crystal can be decreased, and the improvement of oxide-film pressure-proofing of a silicon single crystal can be performed remarkably. And it is not necessary to use an approach which worsens the productivity of a single crystal of reducing the rate of crystal growth extremely, or making a fixed temperature field anneal, and since ultra high-speed raising is possible, the productivity of a single crystal can be raised by leaps and bounds.

[0007] Moreover, invention indicated to claim 2 of this invention is characterized by making it the time amount to which the silicon single crystal raised in the approach of manufacturing a silicon single crystal, by the Czochralski method passes through the temperature region from 1250 degrees C to 1200 degrees C at the time of crystal growth become 20 or less minutes 10 minutes or more. Thus, having limited the lower limit of time amount which passes through the temperature region from 1250 degrees C to 1200 degrees C to invention of claim 1 specifies easily the range of invention which can be attained and which is made more suitable in training of the single crystal in the raising equipment by the general CZ process. Therefore, the range of invention indicated to claim 1 by claim 2 is not limited.

[0008] Furthermore, invention indicated to claim 3 of this invention is the silicon single crystal manufactured by the approach indicated to claim 1 or claim 2. By the approach indicated to said claim 1 and claim 2, since the defective nucleus of the crystal defect which degrades oxide-film pressure-proofing is hard to be formed primarily, the silicon single crystal which has improved oxide-film pressure-proofing certainly can be manufactured.

[0009] Hereafter, although this invention is further explained to a detail, in advance of explanation, lessons is taken from each vocabulary, and it explains beforehand.

1) K2Cr 2O7 after cutting down a wafer from the silicon single crystal rod after growth and etching and removing a surface distortion layer with the mixed liquor of **** and a nitric acid in FPD (Flow Pattern Defect) A pit and a ripple pattern arise by etching a front face with the mixed liquor of fluoric acid and water. This ripple pattern is called FPD, and the defects of oxide-film pressure-proofing increase in number, so that the FPD consistency within a wafer side is high (refer to JP,4-192345,A).

2) Cut down a wafer from the silicon single crystal rod after growth, and carry out cleavage of the wafer to LSTD (Laser Scattering TomographyDefect) after etching and removing a surface distortion layer with the mixed liquor of fluoric acid and a nitric acid. Incidence of the infrared light can be carried out from this cleavage plane, and the defect scattering light which exists in a wafer can be detected by detecting the light which came out from the wafer front face. About the scatterer observed here, it is a society etc., there is already a report, and it is regarded as the oxygen sludge (J. J.A.P. Vol.32, P3679, 1993 reference).

[0010] The defect density of these [FPD] and LSTD is both considered to be an oxide-film proof-pressure degradation factor from there being a percent defective of oxide-film pressure-proofing and strong correlation. Therefore, in order to improve oxide-film

pressure-proofing of the silicon single crystal by the CZ process, it is necessary to decrease this FPD and a LSTD defect.

[0011] When this invention persons did low-speed growth, FPD and LSTD decreased why, and that it should solve whether oxide-film pressure-proofing becomes good, when the growth rate was made to change suddenly at a low speed from a high speed at the time of crystal growth under the structure in [of two kinds such as an annealing mold and a quenching mold] a furnace, the defect density of FPD and LSTD is not from the point changing [growth rate], and it was falling rapidly before [it] (existing growing region). This location that changed changed with structures in a furnace, and was under quenching mold structure in between (A'B from point' point of drawing 1 (a)) about 19-16cm before the point changing [growth rate] the same under annealing mold structure in between (from the A point of drawing 1 (a) to a B point) about 14-11cm before the point changing [growth rate]. However, it turned out that the crystal temperature equivalent to this location is equivalent to a 1150 degrees C - 1080 degrees C temperature zone almost the same (refer to drawing 1 (b)).

[0012] This means that the 1150 degrees C - 1080 degrees C temperature zone under silicon single crystal growth influences as a crystal defect dissipating stage. That is, if the growth rate of a single crystal is reduced extremely, since the crystal under growth will become [pass time] long in all temperature fields and the pass time of a 1150 degrees C - 1080 degrees C temperature region will also become long as a result, when FPD and a LSTD defect pass through a dissipating stage, oxide-film pressure-proofing is improved.

[0013] Therefore, if even pass time of a 1150 degrees C - 1080 degrees C temperature region can be lengthened It is not extinguishing FPD and a LSTD defect, not lengthening pass time of other temperature fields, especially the high temperature region near [which influences the rate of crystal growth directly] the crystal growth interface, and making the temperature gradient near the growth interface tighter. Without dropping the productivity of a single crystal, without [therefore] making the rate of crystal growth into a low speed, it solved that the improvement of oxide-film pressure-proofing could be performed, and proposed previously (Japanese Patent Application No. No. 143391 [seven to]).

[0014] However, although the dissipating stage of FPD and a LSTD defect which degrades oxide-film pressure-proofing as mentioned above solved, if it is unknown about these defective origination of nucleus and formation, this can be solved and formation of the defective nucleus itself can be controlled, the improvement of more perfect oxide-film pressure-proofing of the silicon single crystal by the CZ process can be aimed at. Moreover, although it is not necessary to compare with the former and to reduce a raising rate to the approach of annealing the temperature field of the above-mentioned regularity, so much, it is difficult to desire the raising rate beyond a practical question conventional method, and productivity.

[0015] Then, while this invention persons investigated and solved the temperature field of the defective karyogenesis of the defect used as an oxide-film proof-pressure degradation factor itself further and controlling formation of a defective nucleus, the rate of crystal growth was conventionally made into the high speed, and it examined aiming at achievement of much more quality improvement of a silicon single crystal, and the sex from Takao.

[0016] Carrying out the deer, this invention persons conducted the experiment which makes a growth rate change suddenly from medium speed to ultra high-speed further at the time of crystal growth that this should be solved. Then, the defect density of FPD and LSTD is not from the point changing [growth rate], and it was increasing rapidly before [it] (existing growing region). This location that changed was in between (from C point to D point of drawing 2 (a)) about 22-16cm before the point changing [growth rate]. And the crystal temperature equivalent to this location is equivalent to the 1150 degrees C - 1080 degrees C temperature zone obtained from the above-mentioned experiment (refer to drawing 2 (b)). That is, from the crystal location which begins to quench a 1150 degrees C - 1080 degrees C temperature region, defect density was increasing and it has reconfirmed that the above-mentioned experimental result was right.

[0017] However, when raising of a crystal was continued as it was, the behavior to which defect density decreases again after that was checked. The location where this defect decreased was in between (from E points to F points of drawing 2 (a)) about 12-9cm before the point changing [growth rate]. And it turned out that the crystal temperature equivalent to this location is a thing equivalent to a 1250 degrees C - 1200 degrees C temperature zone (refer to drawing 2 (b)).

[0018] It means that suppose that this is the formation fault of a crystal defect nucleus, and the 1250 degrees C - 1200 degrees C temperature zone under silicon single crystal growth influences. That is, the nucleus is formed in a 1250 degrees C - 1200 degrees C temperature field, and FPD and the LSTD defect which the oxide-film pressure-proofing introduced at the time of growth of a single crystal is degraded follow a dissipating stage in the temperature field which is 1150 degrees C - 1080 degrees C. Therefore, in order to solve more certainly oxide-film pressure-proofing of the silicon single crystal by the CZ process and to make it not make the defective nucleus of FPD and LSTD form at the time of crystal growth, what is necessary will be to quench a 1250 degrees C - 1200 degrees C temperature region as much as possible, and just to shorten the pass time.

[0019] That this should be checked, when this invention persons conducted the still more nearly same experiment under [various] the structure in a furnace and the relation between FPD defect density and the temperature region pass time to 1250 degrees C - 1200 degrees C at the time of crystal growth was investigated, the result as shown in drawing 3 was obtained. When this drawing is seen, it turns out that the crystal with which the time amount which passes through the temperature region to 1250 degrees C - 1200 degrees C is unexceptional as the crystal for 20 or less minutes, there is little defect density, and oxide-film pressure-proofing has been improved is raised. Therefore, if the time amount which passes through this temperature region becomes 20 or less minutes, since the defective nucleus of the oxide-film proof-pressure degradation factor slack FPD and a LSTD defect is formed in a 1250 degrees C - 1200 degrees C temperature region, and a defective nucleus will not fully be formed, the defect density of the crystal made as a result decreases.

[0020] Although dispersion in defect density is large on the other hand when the time amount which passes through a 1250 degrees C - 1200 degrees C temperature region exceeds 20 minutes, there is an inclination for defect density to decrease gradually. Since this had the 1250 degrees C - 1200 degrees C temperature region annealed, many defective nuclei are formed, on the whole, defect density increases, but what has 1250 degrees C - 1200 degrees C long pass time serves as little crystal of defect density gradually in order to also anneal the temperature region of 1150 degrees C - 1080 degrees C of the account of back to front and to follow a defective dissipating stage.

[0021] Thus, according to this invention, in order for the crystal defect in a silicon single crystal to have the temperature region which is 1250 degrees C - 1200 degrees C which is the temperature in which the nucleus itself is formed quenched, a defective nucleation reaction is not enough and the formation is checked. If the defective nucleus is not formed during the crystal, even if what kind of things the subsequent heat history, especially the hysteresis of 1150 degrees C - 1080 degrees C of temperature region slack of a crystal defect dissipating stage are, it is possible to decrease the consistency of an absolute crystal defect, and manufacture of the silicon single crystal of the high quality excellent in the oxide-film proof-pressure property is attained. Furthermore, in this invention, completely conversely, since the conventional method of reducing a raising rate extremely does not need to gather a raising rate extremely and does not need to anneal [and] a fixed temperature region, it can aim at improvement in the fast productivity of a single crystal.

[0022]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained to a detail, referring to a drawing. First, drawing 4 explains the example of a configuration of the crystal-pulling equipment by the CZ process. As shown in drawing 4, this crystal-pulling equipment 100 is equipped with the reel style 109 which rotates or rolls round a chamber 101, the crucible 102 prepared into the chamber 101, the heater 105 arranged around a crucible 102, the crucible maintenance shaft 107 and rolling mechanism 108 which rotate a crucible 102, the seed chuck 22 holding the seed crystal S of silicon, the cable 1 which pulls up a seed chuck 22, and a cable 1, and is constituted. The quartz crucible 103 is formed in the side which holds the melt L inside a crucible 102, and the graphite crucible 104 is formed in the outside of the quartz crucible 103. Moreover, the heat insulator 106 is arranged around [outside] the heater 105. Furthermore, since the flow of the gas in a furnace is prepared and reactant gas, such as SiO to generate, is discharged effectively, the rectification cylinder 2 may be formed so that a growth single crystal may be surrounded. Moreover, by installing the magnet which is not illustrated in the horizontal outside of a chamber 101, and impressing a magnetic field horizontal to silicon melt L to it, the convection current of Melt L is controlled and, recently, the so-called MCZ method for measuring the stable growth of a single crystal is used in many cases.

[0023] Next, the single-crystal-growth approach by above crystal-pulling equipment 100 is explained. First, within a crucible 102, the high grade polycrystal raw material of silicon is heated more than the melting point (about 1400-degreeC), and is dissolved. Next, the tip of a seed crystal S is made contacted or immersed in the surface abbreviation core of Melt L by beginning to roll a cable 1. Then, while rotating the crucible maintenance shaft 107 in the proper direction, single crystal growth is started by rolling round rotating a cable 1 and pulling up a seed crystal S. Henceforth, the single crystal rod C of an approximate circle column configuration can be obtained by adjusting a raising rate and temperature appropriately.

[0024] In this case, in order to improve oxide-film pressure-proofing of a single crystal, using as 20 or less minutes time amount which passes through a 1250 degrees C - 1200 degrees C temperature region like this invention and to raise the productivity of a single crystal by leaps and bounds, it is necessary to compare with the former and to pull up at superhigh speed. Then, while preparing the flow of the gas in a furnace and discharging reactant gas, such as SiO to generate, effectively, in order to make it possible to accelerate the rate of crystal growth by cooling the growth single crystal C and interrupting the radiant heat to a single crystal, the structure in a furnace for carrying out this invention is established so that the rectification cylinder 2 which made the lower limit section approach a melt side may surround a growth single crystal. Since the passage is specified, and inert gas, such as Ar introduced from the upper part of raising equipment by preparing such a rectification cylinder, flows intensively towards a growth single crystal by the rectification cylinder, its effectiveness which cools a crystal is large. And the high-speed growth of a single crystal of such a rectification cylinder is attained more from the ability of the radiant heat from a heater etc. to also be cut [a raw material melt side, a crucible wall, and] further.

[0025]

[Example] Hereafter, the example of this invention is shown.

(Example) With the raising equipment possessing the rectification cylinder shown in drawing 4, 60kg of raw material polycrystalline silicon was charged to the 20 inch quartz crucible, and the diameter of 6 inches and the silicon single crystal rod of bearing <100> were raised at the average raising rate of 1.6 mm/min (body die length of about 85cm of a single crystal rod). The mirror plane wafer of a silicon single crystal was produced by cutting down a wafer and performing mirror plane processing from this single crystal rod. In this way, measurement of said FPD and a LSTD defect was performed about the mirror plane wafer of the made silicon single crystal. The measurement result was shown in the following table 1. In the table, the example of a type of the defect density by the conventional CZ process was written together for the comparison.

[0026]

[Table 1]

	平均成長速度 (mm/min)	F P D (ヶ/cm ²)	LSTD (ヶ/cm ²)
実施例	1.60	$\bar{X}=180$ n= 10	$\bar{X}=2.8 \times 10^5$
比較例 (従来法)	1.00	$\bar{X}=650$ n= 18	$\bar{X}=2.0 \times 10^5$

[0027] In addition, this invention is not limited to the above-mentioned operation gestalt. The above-mentioned operation gestalt is instantiation, and no matter it may be what thing which has the same configuration substantially with the technical thought indicated by the claim of this invention, and does the same operation effectiveness so, it is included by the technical range of this invention. For example, in the above-mentioned operation gestalt, although the example was given and explained per when a silicon single crystal with a diameter of 6 inches was raised, this invention is not limited to this but 20 or less minutes, then the same operation effectiveness are applied also to the diameter of 8-16 inches, or the silicon single crystal beyond it in the time amount which passes through a 1250 degrees C - 1200 degrees C temperature region.

[0028] Moreover, with the above-mentioned operation gestalt, in order to make the growth rate of a single crystal into ultra high-speed, the rectification cylinder was used, but if this invention is not limited to this but can cover raising or radiant heat for the cooling rate of a growth crystal effectively, it will be good also as structure in what kind of furnace. For example, the melt in a crucible and a crucible may be covered partially, radiant heat may be intercepted, and since the cooling effect is increased more in the lower limit section of said rectification cylinder, a thermal shield may be installed in it.

[0029]

[Effect of the Invention] As explained above, FPD of the silicon single crystal manufactured by the CZ process and a LSTD defect can be decreased by this invention, and the crystal of the high quality which was excellent in oxide-film pressure-proofing can be obtained. And in this invention, since a raising rate is fallen extremely, or a fixed temperature field does not need to be annealing-ized etc. but a crystal is pulled up at superhigh speed, the productivity of a single crystal can be raised by leaps and bounds.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) It is drawing having shown the relation of the crystal location and FPD defect density at the time of making a low speed sudden-change-size a growth rate among crystal growth.

(b) It is drawing having shown the relation between the distance from the surface of hot water, and crystal temperature.

[Drawing 2] (a) It is drawing having shown the relation of the crystal location and FPD defect density at the time of making a high speed sudden-change-size a growth rate among crystal growth.

(b) It is drawing having shown the relation between the distance from the surface of hot water, and crystal temperature.

[Drawing 3] It is drawing having shown the relation between the pass time from 1250 degrees C to 1200 degrees C, and FPD defect density.

[Drawing 4] It is the cross-section schematic diagram of the crystal-pulling equipment by the CZ process.

[Description of Notations]

1 Cable 2 Rectification Cylinder

22 Seed Chuck

100 Crystal-Pulling Equipment 101 Chamber

102 Crucible 103 Quartz Crucible

104 Graphite Crucible 105 Heater

106 Heat Insulator 107 Crucible Maintenance Shaft

108 Rolling Mechanism 109 Reel Style

C Growth single crystal

L Silicon melt

S Seed crystal

[Translation done.]

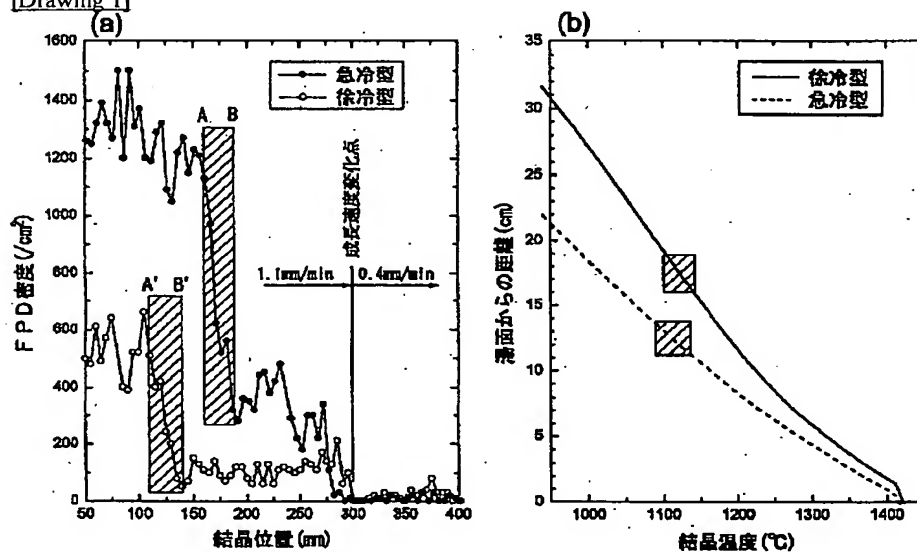
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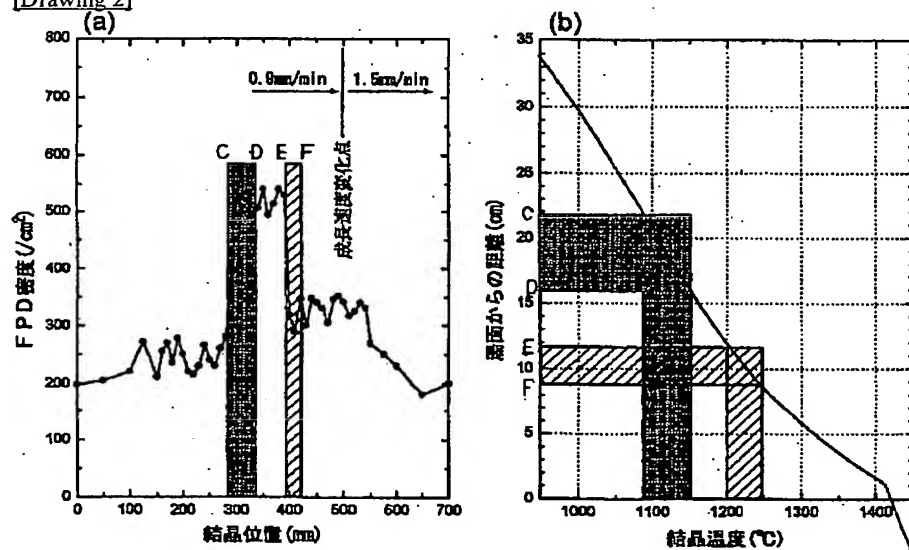
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DRAWINGS

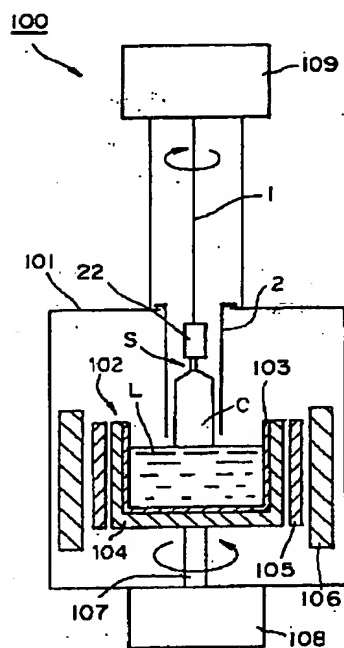
[Drawing 1]



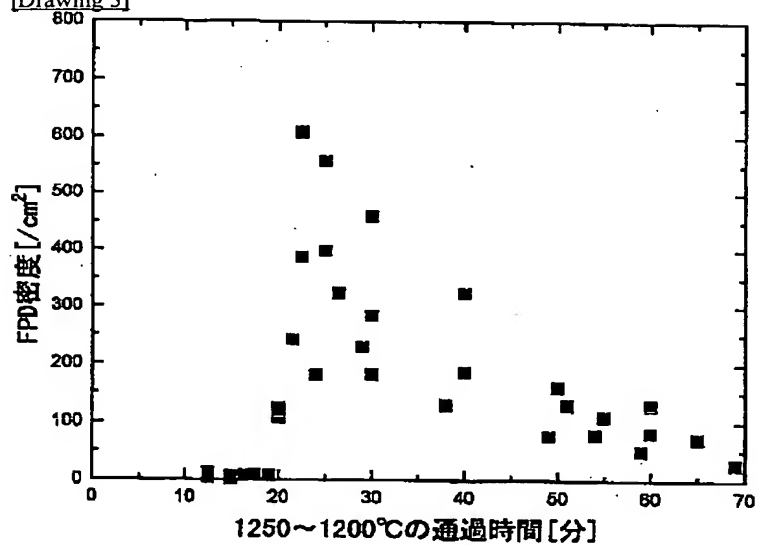
[Drawing 2]



[Drawing 4]



[Drawing 3]



[Translation done.]

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